

If parabolas with vertical axes (Callendar) be described through the points (1) B, C, D; (2) C, D, E; (3) C, D, F, they will be different, since the curve of observation is not itself parabolic. In the case of these parabolas, where the resistances at C and D are common to all, the product of  $\delta$  and the parameter (P) of the corresponding parabola is constant; hence the smaller  $\delta$  becomes, the more open—or less curved—will be the parabola along the arc we have to deal with. This result is in accordance with the curve in fig. 2, and explains why, as I have already pointed out, the two parabolas for high and low temperatures are not only different, but also may differ from each other by any amount, within certain limits depending on the nature of the unknown curve of temperature and resistance.

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“Physical Constants at Low Temperatures. (1)—The Densities of Solid Oxygen, Nitrogen, Hydrogen, etc.” By Professor JAMES DEWAR, M.A., LL.D., D.Sc., F.R.S. Received March 9, —Read March 17, 1904.

1. The following experiments on the solid densities of oxygen, nitrogen and hydrogen were carried out as part of a former investigation dealing with gaseous densities at low temperatures.\*

The method adopted was to measure the volumes of the gases sucked into a cooled space of known capacity, when the temperature was such as in the first place to induce liquefaction and finally solidification. For such experiments to be successful the rate of liquefaction and the cooling must be under thorough control, otherwise the cooled space may not get completely filled with solid. Further, the volume of gas condensed ought to be as large as possible, in any case about 20 litres, in order to diminish errors inseparable from the mode of manipulation. The inertia of the bell-jars of the large gas-holders causes some variation in the pressure; and errors of their calibration, and want of uniformity of temperature in the mass of gas, are all important factors. As my object was to ascertain experimentally the limiting density in the solid state, the elimination of these variations was not so important as it would have been for the study of fluid density.

The dry purified gas was contained in a gas-holder connected by a pipe with a glass bulb of 20 or 30 c.c. capacity, sealed to a narrow tube some 10 cm. long, with a glass stop-cock at the end. The

\* “The Specific Volumes of Oxygen and Nitrogen Vapour at the Boiling Point of Oxygen,” ‘Roy. Soc. Proc.’ vol. 69.

glass bulb was immersed in liquid oxygen, nitrogen, or hydrogen contained in a vacuum-jacketed vessel with arrangements for lowering the temperature of the liquids by exhaustion. The narrow tube just above the glass bulb had a mark engraved upon it, and the volume up to this point, which is to be filled with liquid or solid after cooling, was antecedently carefully calibrated. The glass stop-cock on the projecting part of the glass tube outside the vacuum vessel enabled the rate of the gas supply to be under complete control. The real difficulties were those of manipulation.

The temperatures employed were the boiling point of oxygen,  $90^{\circ}5$ ; the boiling point of nitrogen,  $77^{\circ}5$ ; the melting point of nitrogen,  $62^{\circ}5$ ; the boiling point of hydrogen,  $20^{\circ}5$ ; hydrogen boiling under 76 mm. of pressure taken as  $14^{\circ}7$ ; and hydrogen (solid) under 10 mm. of pressure taken as  $13^{\circ}1$ .

Allowance for the contraction of the bulb was made by taking 0.0000250 as the coefficient of contraction (cubical) of the glass. It is possible that in going to very low temperatures (below  $-200^{\circ}$  C.), this coefficient ought to be less, such as 0.0000225. An estimate made of the difference between the two would come within the range of errors, consequently the former value which was adopted in the earlier investigations was retained.

The weight of 1 litre of oxygen at  $0^{\circ}$  C. under 760 mm. pressure was taken as 1.430 grammes, of nitrogen as 1.2564 grammes, and of hydrogen as 0.0899 gramme.

The observations and results are given in the following tables:—

Table I.—Oxygen.

No.	Description.	T'.	V.	T.	p.	d.
					mm.	
1	At B.P. of O ..	$-182^{\circ}5$	19.631	$14^{\circ}4$	758.5	1.1181
2	At B.P. of N ..	$-195^{\circ}5$	20.536	$14^{\circ}4$	758.5	1.1700
3	At M.P. of N ..	$-210^{\circ}5$	21.743	$14^{\circ}55$	758.5	1.2386
4	At B.P. of H ..	$-252^{\circ}5$	25.003 (solid)	$14^{\circ}6$	758.5	1.4256

Where T' = the temperature Centigrade of the condensed gas in the flask at the time of observation.

V = volume of gas in litres at temperature T° C. and pressure p. mm.

d = density of the condensed gas at T° C.

The volume of the flask at  $15^{\circ}$  C. was 23.9212 c.c.

Coefficient of expansion of glass, taken as 0.0000250.

Weight of 1 litre of oxygen at  $0^{\circ}$  C. and 760 mm., taken as 1.430 grammes.

Table II.—Nitrogen.

No.	Description.	T'.	V.	T.	p.	d.
					mm.	
1	At B.P. of N ..	-195°·5	15·192	16°·1	747	0·8042
2	At M.P. of N ..	-210·5	16·592	15·95	747	0·8792
3	At B.P. of N ..	-252·5	18·911 (solid)	14·65	761	1·0265

The same notation is used as in Table I.

The volume of the flask at 14°·2 C. was 22·1454 c.c.

Coefficient of expansion of glass, 0·0000250.

Weight of 1 litre of nitrogen at 0° C. and 760 mm., 1·2564.

Table III.—Hydrogen.

No.	Description.	T'.	V.	T.	p.	d.
					mm.	
1	At B.P. of H ..	-252°·5	18·051	14°·6	760	0·0700 $\frac{1}{2}$
2	H under 76 mm.	-258·29	19·447	14·6	760	0·0754 $\frac{1}{2}$
3	H under 10 mm.	-259·9	19·597 (solid)	14·3	762	0·0763

The same notation is used as in Table I.

The volume of the flask at 14°·2 C. was 22·1454 c.c.

Coefficient of expansion of glass, 0·0000250.

Weight of 1 litre of hydrogen at 0° C. and 760 mm., taken as 0·0899.

2. It is of advantage to estimate the effects of an error, or of any reading that may have been taken roughly. Taking the notation already employed, and putting  $w$  for the weight of 1 litre of the gas at 0° C. and 760 mm., then the weight of gas used is

$$W = \frac{Vp273}{760(273+T)} w;$$

and if  $V_0$  be the volume of the flask up to the mark at some ordinary temperature  $T_0$ ° C., and  $V'$  its volume at  $T'$  the temperature Centigrade of the observations, then

$$V' = V_0 \frac{1+\beta T'}{1+\beta T_0},$$

where  $\beta$  is the cubical coefficient of expansion of the glass. Hence, the density of the substance at the time of observation is

$$d = \frac{W}{V} = \frac{Vp273w}{760(273+T)} \times \frac{1+\beta T_0}{V_0(1+\beta T')},$$

or, with sufficient accuracy for our investigation,

$$d = \frac{273w}{760V_0} \times \frac{Vp(1+\beta T_0 - T')}{273+T} \dots\dots\dots (1).$$

An important error might be expected to arise from an inaccurate knowledge of  $T'$  the temperature of the cooled gas. An alteration of a degree in the value of  $T'$  would alter the value of  $d$  by

$$-\frac{273w}{760V_0} \times \frac{Vp}{273+T} \beta,$$

or very approximately, a rise of a degree in the estimate of  $T'$  above its true value would diminish  $d$  by  $\beta d$ —in the present case by  $\frac{1}{40000}$  part.

Similarly an error of a degree in the estimate of the temperature  $T_0$ , at which the volume of the flask was measured, would have the like small effect, but in the opposite direction.

On the other hand errors in the measurements of either  $V$  or  $V_0$  or of  $p$  or  $T$  would give directly proportional errors in the value of  $d$ . The values of  $T$  were easily read to one-tenth of a degree, so that an error in this quantity would have an effect less than  $\frac{1}{30000}$  on the value of  $d$ . Similarly the pressure was read to  $\frac{1}{2}$  mm., leaving an error of less than  $\frac{1}{15000}$  on the density. The volume  $V$  showed a tendency to error in the earlier portion of each group of experiments, but this was eliminated as the experiments progressed and especially where the results were more important, namely, in the region of the solidified gases. The greatest care was taken to insure that the whole volume of the bulb was occupied by the solid. The gas was allowed to enter in successive portions, each of which was liquefied and solidified previous to any further admission, so as to insure the absence of any vacua due to contraction.

3. The results for oxygen seem low, the boiling-point density being 1.118, whereas former results gave 1.138. On plotting the densities as ordinates to the temperatures as abscissæ the observations lie very closely on a straight line which (by least squares), is

$$d = 1.5154 - 0.004420t \dots\dots\dots (2),$$

$t$  being absolute temperature.

Such a line as (2) must in any case be only a chord of the curve of liquid densities, and the nearer two observations are to the absolute zero, the more nearly will the chord joining them partake of the nature of a tangent to this curve at the absolute zero. Now, at so low

a temperature as  $20^{\circ}\cdot 5$  for oxygen we may consider its gaseous density to be practically negligible. Hence one point on Matthias's rectilinear diameter for oxygen will be, at  $20^{\circ}\cdot 5$ , a density equal to  $0\cdot 7128$ , the half of that given in No. 4, Table I. In former papers I found the density of liquid oxygen at its boiling point to be  $1\cdot 138$ , and of gaseous oxygen at the same point to be  $0\cdot 00440$ ; half the sum of these is  $0\cdot 5712$ , which gives another point on Matthias's diameter at  $90^{\circ}\cdot 5$ . Thus Matthias's diameter for oxygen is

$$d = 0\cdot 7543 - 0\cdot 002023t \dots\dots\dots (3),$$

and taking the critical temperature as  $155^{\circ}$  absolute, we get the critical density to be  $0\cdot 4407$ , agreeing notably with the usually accepted value  $0\cdot 44$ . The inference from this is that the density of solid oxygen at the boiling point of hydrogen is  $1\cdot 4256$ .

The results for nitrogen, taken at three temperatures, do not warrant the deduction of a linear relation between  $d$  and  $t$ , especially as on plotting the observations the concavity of the liquid density curve though slight is quite apparent. However, there are two observations at temperatures so low that the corresponding gaseous densities may be neglected, thus enabling us to construct a Matthias diameter. At the boiling point of hydrogen, the ordinate of the Matthias line is therefore very nearly  $\frac{1}{2} (1\cdot 0265) = 0\cdot 5133$ ; similarly at the melting point of nitrogen the ordinate is  $\frac{1}{2} (0\cdot 8792) = 0\cdot 4396$ . Hence the Matthias diameter is

$$d = 0\cdot 5492 - 0\cdot 00175t \dots\dots\dots (4),$$

which for the critical temperature  $127^{\circ}$  gives the critical density as  $0\cdot 3269$ . This agrees very well with the value deduced by Matthias\* from Wroblewski's liquid densities, namely  $0\cdot 333$ , though it is somewhat higher than the value  $0\cdot 299$  which he deduced from the theory of corresponding states.†

Only three observations have been obtained for hydrogen, which again lie nearly on a straight line, but nevertheless present a very slight concavity to the axis of temperature. If we treat the two lowest densities as we have done with nitrogen, we get for the Matthias diameter the line

$$d = 0\cdot 04136 - 0\cdot 000247t \dots\dots\dots (5),$$

whence the annexed table (p. 256) of critical densities according to the temperatures chosen for the critical temperatures. Berthelot gives an estimate for the critical density as  $0\cdot 033$ , and quotes Wroblewski's critical temperature as  $33^{\circ}$ , two results closely in accord with the numbers in this table. We are, therefore, justified in considering

\* 'Mem. Soc. Roy. des. Sci. de Liège,' 3rd Series, 1899.

† 'Le point critique des corps purs,' p. 176.

<i>tc.</i>	<i>dc.</i>
28°	0·03444
29	0·03420
30	0·03395
31	0·03370
32	0·03346
33	0·03321
34	0·03296

these hydrogen densities as very closely in agreement with facts, the density at the boiling point coinciding nearly with my former determinations.

4. Assuming that vapour densities at very low temperatures may be neglected in comparison with corresponding liquid densities, the Matthias diameter enables us to approximate to the molecular volumes of the condensed gases at the absolute zero. For if  $d' = a - bt$  be the equation of Matthias's diameter, then  $d = 2a - 2bt$  is very approximately the tangent of the liquid density curve near the absolute zero, and therefore  $1/2a$  is the specific volume at absolute zero.

Hence from the above equations for Matthias's diameter, if  $V_0$  = the molecular volume at absolute zero, we have  $V_0 = 21\cdot21$  for oxygen,  $V_0 = 25\cdot49$  for nitrogen, and  $V_0 = 24\cdot18$  for hydrogen. The oxygen and nitrogen molecular volumes at absolute zero probably err by defect; but the hydrogen result must be taken as very near the true value.

We may compare these values with the results of theoretical investigation. Guldberg\* gives for the molecular volume at zero of oxygen 21·5, and of nitrogen 23·6; and Berthelot's† values for the same gases respectively are 20·8 and 25·0. From Baly and Donnan's‡ equations for oxygen, nitrogen, carbonic oxide and argon, deduced from observations within the range of temperature 69°—90° absolute, we find the following values for the molecular volumes at absolute zero: oxygen 20·30; nitrogen 24·04; carbonic oxide 24·54; argon 20·34.

Again, the Waterston-Avenarius formula connecting temperature and fluid volume, namely,

$$v = c - d \log (A - t) \dots\dots\dots (6),$$

where  $A$  is the critical temperature, gives the following equations, from Baly and Donnan's results,

\* 'Zeit. f. Phys. Chem.,' 1895, vol. 16, p. 7.

† 'Comptes Rendus,' March, 1900.

‡ 'Journ. Chem. Soc.,' July, 1902, pp. 911—914.

Oxygen .....	$v = 1.9305 - 0.5838 \log (154 - t),$ $V_0 = 20.90, \quad c/d = 3.3.$
Nitrogen .....	$v = 2.5659 - 0.7868 \log (127 - t),$ $V_0 = 25.80, \quad c/d = 3.27.$
Carbonic oxide .....	$v = 2.6181 - 0.7948 \log (133 - t),$ $V_0 = 26.04, \quad c/d = 3.29.$
Argon.....	$v = 1.6331 - 0.5026 \log (155 - t),$ $V_0 = 21.30, \quad c/d = 3.70.$

This same formula has been adopted by Mallet and Friderich,\* subject to the modification that  $A$  is a unique temperature to be determined for each substance from experiment. On applying it to twenty-five substances, studied by Sydney Young, they find that  $A$  is somewhat higher than the critical temperature and that  $c/d$  is always very nearly equal to 3.78. Baly and Donnan's observations give rise to these Waterston-Mallet equations:—

Oxygen .....	$v = 3.88413 - 1.3604 \log (253 - t),$ $V_0 = 19.68, \quad c/d = 2.86.$
Nitrogen .....	$v = 3.1563 - 1.0560 \log (143.67 - t),$ $V_0 = 24.58, \quad c/d = 2.99.$
Carbonic oxide ...	$v = 4.60090 - 1.64207 \log (191.1 - t),$ $V_0 = 23.94, \quad c/d = 2.80.$
Argon .. .....	$v = 0.98285 - 0.19263 \log (112.4 - t),$ $V_0 = 23.52, \quad c/d = 5.10.$

With assumed values for  $A$ , in the neighbourhood of the range of temperature in which we look for the critical temperature, two Waterston-Mallet formulæ were constructed for hydrogen based on the results of Table III, namely:—

$$v = 23.22 - 7.536 \log (36.5 - t), \quad V_0 = 22.90,$$

$$v = 26.83 - 9.592 \log (41.5 - t), \quad V_0 = 22.62.$$

Assuming that for liquids Van der Waals's equation may be written

$$\frac{Rt}{v-b} = \frac{a}{v^2} \dots\dots\dots (7),$$

an assumption which has been employed by G. N. Lewis† and others, the results of Table III give for hydrogen, with this equation,  $b = 11.56$  and hence  $V_0 = 23.12$ .

For comparison these values may be arranged in tabular form thus:—

\* 'Arch. Sci. Phys. et Nat.,' July, 1902.

† 'Amer. Acad. Arts and Sci.,' 1900, vol. 35, pp. 1—27.

	O.	N.	H.	CO.	Arg.
Present experiments.....	21·21	25·49	24·18	..	..
Guidberg .. .. .	21·50	23·6	..	..	..
Berthelot .. . . .	20·8	25·0	..	..	..
Baly, Linear.....	20·30	24·04	..	24·54	20·34
Baly, Waterston.....	20·90	25·80	..	26·04	21·30
Baly, W.-Mallet .....	19·68	24·58	..	23·94	23·52
W.-Mallet, for H.....	..	..	22·90	..	..
W.-Mallet, for H.....	..	..	22·62	..	..
Lewis.....	..	..	23·12	..	..

The two Waterston-Mallet results for hydrogen are of importance as showing that even great variations in the value of  $A$  affect but little the zero molecular volume. It is further to be remarked that the hydrogen results claim precedence over the others because they have been obtained from observations extending down to some  $14^\circ$  absolute. Moreover, the value 24·18 for hydrogen has been got directly from experiment, whilst the other values have been obtained from semi-theoretical equations whose validity is subject to some doubt.

5. With these values for the molecular volumes at absolute zero of oxygen, nitrogen and hydrogen, namely 21·21, 25·49 and 24·18 respectively, and knowing that the molecular volume of ice at absolute zero is 19·21 and of carbonic acid is 25·7 as deduced from a study of the coefficients of expansion at low temperatures,\* we can find the contraction or expansion on the assumed hypothetical production of these compounds from their elements at the zero of temperature.

Thus 100 volumes of mixed solid hydrogen and oxygen become after combination 55·22 volume of ice, or there is a contraction of 45 per cent. This is of the same order of magnitude as for  $N_2O$  and  $Li_2O$ , whose contraction from solid oxygen, solid nitrogen and metal amounts to 60 per cent. On the other hand the production of carbonic acid from diamond ( $V_0 = 6·82$ ) or graphite ( $V_0 = 10·44$ ) and solid oxygen gives in the former case a slight expansion of  $4\frac{1}{3}$  per cent., but in the latter case a slight contraction of 3 per cent.

The case of carbonic oxide ( $V_0 = 24·5$ ) is interesting; produced from diamond and oxygen it expands by  $74\frac{3}{4}$  per cent., and from graphite and oxygen it expands by  $54\frac{3}{4}$  per cent., but on the addition of another atom of oxygen the resulting product, carbonic acid, undergoes a contraction of 27 per cent.

6. Berthelot† made a minute examination of the values of  $d(pv)/dp$  in reduced co-ordinates for eight substances whose critical temperatures

\* "Coefficients of the Cubical Expansion of Ice, Hydrated Salts, Soluble Carbonic Acid, and other Substances at Low Temperature," 'Roy. Soc. Proc.,' vol. 73.

† "Sur les Thermomètres à gaz. Trav. et Mém. Poids et Mesures," vol. 13.



range from that of carbonic acid to that of hydrogen; and came to the conclusion that the co-volume is one quarter of the critical volume, at least for low pressures.

Guldberg\* from a careful graphical discussion of Young's results arrived at the conclusion that the critical volume is 3.55 times the volume at absolute zero.

An independent examination of the reduced curve for Young's fluor-benzene showed that the reduced volume for a reduced pressure between 0.05 and 0.10 is very approximately 0.4, in other words, that the critical volume is two and a half times the co-volume. And it is to be noted that the variations of the reduced volume in this neighbourhood are very slight compared with the change of the reduced pressure. Further, this range of reduced pressure will cover the extent of the present experiments whatever may eventually prove to be the value of the real critical pressure. My old experiments gave as a maximum a critical pressure of a little over 15 atmospheres.

Hence taking Van der Waals's  $b = 12$  for hydrogen, these results give respectively 48 c.c., 42.6 c.c. and 30 c.c. as the critical volume, with the corresponding critical densities, 0.0208, 0.0235, and 0.033.

What further considerations can be brought to determine between these results? Van der Waals gives, for corresponding states of two bodies, the equation†

$$\frac{d}{d'} = \frac{M}{M'} \frac{p_c}{t_c} \frac{t'_c}{p'_c},$$

where  $d$  is density and  $M$  is molecular weight. Now in the liquid states for moderate pressure, the density changes but slightly, hence we may assume with very little error that the boiling-point densities belong to corresponding states. Comparing, therefore, hydrogen with oxygen, we get:—

$$\frac{0.070}{1.138} = \frac{2}{32} \frac{p_c}{t_c} \frac{155}{50} \text{ or } \frac{t_c}{p_c} = 3.15;$$

and comparing hydrogen with nitrogen we have,

$$\frac{0.07}{0.79} = \frac{2}{28} \frac{p_c}{t_c} \frac{127}{35} \text{ or } \frac{t_c}{p_c} = 2.93,$$

hence, taking the mean, we have for hydrogen  $t_c/p_c = 3.04$ . Now, Van der Waals's theory makes  $p_c v_c/t_c = \frac{3}{8} R$ , but experiment seems to require  $p_c v_c/t_c$  to be equal to  $\frac{1}{3.77} R$ , and when  $p$  is measured in atmospheres,  $R = 41.0183$  for hydrogen, for which, therefore,

$$\frac{p_c v_c}{t_c} = \frac{41.0183}{3.77} = 10.8801.$$

\* *Loc. cit.*

† "Continuity, &c." (English translation), p. 491.

This gives  $v_c = \frac{10.8801}{3.0} = 35.08$  and the critical density as 0.0285, a result midway between that got from Guldberg's ratio and that derived from Young's reduced fluor-benzene.

Further experimental results can be brought to bear on the question. I have recently measured directly the heat of vaporisation of liquid hydrogen at the boiling point and find it to be not more than 125 calories per gramme. Assuming the Rankine equation  $\log_{10} p = A - B/t$ , the molecular heat of vaporisation is  $2B \log_e 10$ . Hence we get  $B = 54.34783$ ; and determining  $A$  from the values of  $p$  and  $t$  at the boiling point we have in atmospheres,

$$\log_{10} p = 54.34783 \left( \frac{1}{20.5} - \frac{1}{t} \right).$$

Now, at the critical point we have found  $t_c = 3.04 p_c$ , hence combining these results we have finally,

$$t_c = 33.88^\circ, \text{ and thence } p_c = 11.145 \text{ atmospheres.}$$

Before leaving these results we may write the Rankine equation in Van der Waals's form, namely,

$$-\log \epsilon = \frac{54.34783}{t_c} \frac{1-m}{m},$$

where  $\epsilon$  and  $m$  are the reduced pressure and temperature, and Van der Waals's  $f$  is  $54.34783/t_c$ , or with the above result, 1.604, about half the usual value of  $f$ . In like manner Trouton's constant, namely, the ratio of the molecular latent heat to the absolute temperature of the boiling point, is  $125/20.5$  or 6.096, again only about half the usual value.

In this connection we may refer to Olzewski's experimental observation of the temperature,  $192^\circ$  absolute, at which the Joule-Thomson effect vanishes when the expansion is from a great pressure, in this instance between 110 and 117 atmospheres. With the usual Van der Waals's notation we may express the connection between this inversion temperature and the critical temperature in either of the forms,

$$t = \frac{27}{4} \left( \frac{v-b}{v} \right)^2 \cdot t_c \dots\dots\dots (9),$$

or

$$t = 3 \left( 1 + \frac{1}{2} \sqrt{1 - \frac{p}{9p_c}} \right)^2 \cdot t_c \dots\dots\dots (10),$$

the former equation shows that for small pressures and consequent values of  $v$  so great that  $b$  may be neglected in comparison with  $v$ , the critical temperature is  $4/27$  of the temperature of inversion. But

when the pressure is great, the ratio  $b/v$  cannot be neglected and the critical temperature is a greater multiple of the temperature of inversion. The second of these equations shows that the initial pressure must not exceed nine times the critical pressure. Assuming a critical pressure of 16 atmospheres for hydrogen and taking  $p = 117$  atmospheres and  $t = 192^\circ$ , this equation gives the critical temperature as  $42^\circ$  absolute. Again, for  $p_c = 15$  atmospheres,  $t_c = 46^\circ$  and for  $t_c = 32^\circ$ ,  $p_c = 41$  atmospheres.

Results derived from a discussion of similar equations depending on Clausius's formula, Berthelot's "modified" Van der Waals's, or Reinganum's formula, are still farther from the value we expect.

In part explanation of this failure it is to be noted that these formulæ are but the best theoretical approximations we have at hand, and while they are useful within short ranges, we can hardly expect the same accuracy over a temperature range of five or six times the critical temperature.

Again, for a very large number of bodies the product of  $\alpha$ , the co-efficient of expansion at the boiling point, and the critical temperature is constant and about 0.6 to 0.7.

Thus for oxygen from equation (2), we have  $\alpha t_c = 0.61$ . For nitrogen we get  $\alpha t_c = \frac{0.0750}{0.8042 \times 15} \times 127 = 0.79$ , but for hydrogen we have  $\frac{0.0054}{0.07 \times 5.8} \times 34 = 0.45$  and even if we take the critical temperature as high as  $42^\circ$ ,  $\alpha t_c$  only reaches 0.56.

7. There are, therefore, as far as we can see at present, and as far as theoretical considerations can aid us, great departures shown by hydrogen from what are fairly general results. Van der Waals's  $f$  and Trouton's constant are each only about half the usual values; and we have now found, from the consideration of the point of inversion of the Joule-Thomson effect, and of the product  $\alpha t_c$ , variations greater than the average from the values we should have expected. Further experiment will be necessary before these discrepancies can be cleared up.